



Network formation of nanofibrillated cellulose in solution blended poly(methyl methacrylate) composites

Kuisma Littunen, Ulla Hippi, Tapio Saarinen, Jukka Seppälä*

Polymer Technology, Department of Biotechnology and Chemical Technology, Aalto University School of Chemical Technology, P.O. Box 16100, 00076 Aalto, Finland

ARTICLE INFO

Article history:

Received 9 May 2012

Received in revised form 20 July 2012

Accepted 9 August 2012

Available online 18 August 2012

Keywords:

Nanofibrillated cellulose

PMMA

Nanocomposite

Percolation

Graft copolymerization

ABSTRACT

Composites of poly(methyl methacrylate) (PMMA) and nanofibrillated cellulose (NFC) were prepared by solution blending and further processed by injection and compression molding. To improve adhesion at the PMMA/NFC interface, the nanofibrils were covalently grafted with PMMA. Formation of a percolating nanofibril network was observed between 1 and 5 wt.% of NFC by dynamic rotational rheometry in molten state. This observation was further supported by the behavior of glass transition temperature which decreased at low NFC concentrations but recovered above the percolation threshold, indicating a decreased mobility of the matrix polymer. This effect was more pronounced with ungrafted NFC, possibly due to a stronger network. The unmodified NFC induced a minor degradation of the molar mass of PMMA. As thin plates, the composites were transparent at low NFC concentrations but became partially aggregated at the highest NFC concentrations. Despite the continuous NFC network, tensile testing showed no improvement of the mechanical properties.

© 2012 Elsevier Ltd. All rights reserved.

1. Introduction

Nanofibrillated cellulose (NFC) is a wood-based nanomaterial, prepared from pulp by mainly mechanical grinding or fluidization, sometimes combined with chemical or enzymatic pretreatments. The fibrils are below 100 nm in diameter and up to several micrometers long. Their specific surface area is also very large due to the small diameter and large aspect ratio (Pääkkö et al., 2007; Turbak, Snyder, & Sandberg, 1983). NFC has attracted increasing attention during the past decade because of its many unique properties. Due to the low amount of structural defects, the mechanical strength of an individual nanofibril is far superior to a pulp fiber, approaching the properties of a perfect cellulose crystal. The high strength and expanded surface area make NFC a promising reinforcement material for polymer composites (Helbert, Cavailé, & Dufresne, 1996). Another interesting feature of NFC is its tendency to form a continuous, web-like network of interconnected nanofibers in suspensions already at very low concentrations (Pääkkö et al., 2007). In polymer composites, the network can increase toughness by preventing crack propagation. Composites reinforced with NFC have exhibited significantly higher tensile strength and elongation at break, compared to corresponding pulp fiber composites (Nakagaito & Yano, 2005). The fibril diameter, being far below the wavelength of visible light, also enables the reinforcement of transparent

polymers without compromising their optical properties. Moreover, the transparency of nanocomposites is highly insensitive to the refractive indices of the components and therefore also to temperature variations (Nogi, Handa, Nakagaito, & Yano, 2005).

The main challenges in composite applications are associated with the high hydrophilicity of cellulose, which makes it incompatible with many bulk polymers (Berglund, 2005). One approach to improve the adhesion in NFC composites is the grafting of synthetic polymers from the NFC surface. Covalently attached polymer layer increases adhesion between solid surfaces due to entanglements (Nordgren, Lonnberg, Hult, Malmstrom, & Rutland, 2009), suggesting that graft copolymerized cellulose also has stronger affinity to a surrounding polymer matrix. These copolymers are simple to synthesize by using several acrylic monomers (Littunen et al., 2011).

Poly(methyl methacrylate) (PMMA) is a glass-clear polymer which has many uses in optical applications. Its applicability is limited by the relatively low mechanical strength and susceptibility to scratching. To reinforce PMMA, it has been blended with natural and modified cellulose fibers by melt compounding. The grafting approach has been tested in order to improve the adhesion between the fibers and the polymer, by using cellulose fibers grafted with PMMA and poly(butyl acrylate) (PBA) (Canché-Escamilla et al., 2002). Addition of cellulose grafted with PMMA resulted in slightly higher elastic modulus, while the addition of PBA grafted cellulose made the composite less rigid and improved the impact strength notably. However, relatively high amounts of fiber were needed for these improvements, leading to deterioration of the tensile strength.

* Corresponding author. Tel.: +358 9 4702 2614; fax: +358 9 462 373.
E-mail address: jukka.seppala@aalto.fi (J. Seppälä).

Melt blending is a very common method to make polymer composites but it has been found to be problematic in the preparation of cellulose nanocomposites because nano-sized cellulose forms strong aggregates during drying that are not properly redispersed during the melt processing. The other possibility is to feed NFC into extruder as a water suspension. In this case, there is a risk of foaming due to the evaporating water (Bondeson & Oksman, 2007). Moreover, the presence of water at high temperatures can be detrimental to polymers containing e.g. amide or ester bonds (Taubner & Shishoo, 2001). For these reasons, we wanted to investigate the possibility to mix NFC suspension with dissolved polymer, which allows efficient drying of NFC with less aggregation and enables also the mixing of the components before molding.

Solution blending has been studied by impregnating regenerated cellulose films with dissolved PMMA over a wide concentration range. A linear increase in modulus and tensile strength was observed with increasing cellulose content in PMMA composites, approaching the values of pure cellulose (Isobe, Sekine, Kimura, Wada, & Kuga, 2011).

Only few studies have been published on mixing nano-sized cellulose with PMMA. Cellulose nanocrystals (CNC) have been used in composites prepared by solution blending and subsequent casting into transparent sheets by evaporating the solvent (Liu, Liu, Yao, & Wu, 2010), and by electrospinning into sub-micron sized fibers (Dong et al., 2012). In both cases, the storage modulus was found to increase with the addition of CNC, but the effect on the tensile properties of PMMA was not determined.

In this paper, we report the preparation of PMMA/NFC composites by solution blending. By using cellulose nanofibers instead of nanocrystals, it was possible to study also the network-forming behavior of NFC. To investigate the possible contribution of the grafted polymer to the interfacial adhesion and network strength, both unmodified and PMMA-grafted NFC were used in the composites. The gel character of the materials in molten state was determined by dynamic rotational rheometry and the effect of NFC to the mobility of the polymer chains was studied by dynamic scanning calorimetry (DSC). Information about adhesion, transparency, and dispersion was collected by visible light transmittance measurements and mechanical testing of the composites.

2. Experimental

2.1. Materials

Nanofibrillated cellulose was provided by UPM Corporation (Helsinki, Finland) with a product name UPM Fibril Cellulose. The material was prepared by mechanical disintegration of bleached birch pulp, which was pre-treated with a Voith refiner and then fluidized by seven passes through an M7115 fluidizer (Microfluidics Corp, Newton, MA, USA). The solids content of the prepared water dispersion was 1.6 wt.%. Tetrahydrofuran (THF, analytical grade) was purchased from VWR (Karlskoga, Sweden) and PMMA ($M_n = 70$ kg/mol) from LG Chem (Seoul, South Korea).

2.2. Graft copolymerization

The grafting of NFC was carried out by free radical graft copolymerization with methyl methacrylate (MMA) in aqueous suspension. The method was described in detail in our earlier article, and the product used in this study was identical to the NFC-PMMA 4 batch reported therein (Littunen et al., 2011). The polymerization time was 60 min, 2 mmol/dm³ of cerium (IV) ammonium nitrate (CAN) was used as initiator, and the amount of monomer was 40 mmol/g of dry NFC. Simultaneously formed homopolymer was removed from the product by washing with

THF. The PMMA content of the grafted NFC, determined gravimetrically, was 49 wt.%. The grafted polymer was isolated by hydrolyzing the cellulose backbone with sulfuric acid and its molar mass was measured by gel permeation chromatography (GPC). The number average molar mass of the grafted PMMA was 127,000 g/mol, and its polydispersity index (PDI) was 1.88.

2.3. Solution blending

Commercial PMMA (10 g) was dissolved in THF as 15 wt.% solution, and never-dried NFC (neat or grafted) was centrifuged and redispersed twice in acetone and then three times in THF. The NFC suspension was poured into the PMMA solution to yield a concentration of 0.5, 1.0, 5.0 or 15 wt.% of dry cellulose. The mixture was agitated by a magnetic stirrer until no visible aggregates were observed, and dried at ambient temperature.

2.4. Preparation of the test specimens

Materials were dried at 60 °C overnight before molding. Plates of 0.5 mm in thickness were compression molded at 210 °C with a TP 400 plate press (Fontijne Grotnes BV, Vlaardingen, Netherlands) for evaluation of transparency and melt rheology. Tensile test bars were prepared with a mini-injection molding machine (DSM, Heerlen, Netherlands). The temperature of the injection cylinder and the mold were 230 and 100 °C, respectively.

Tensile properties were characterized with an Instron 4204 testing machine (Norwood, MA, USA) with a test speed of 2 mm/min. The specimen type was 1.5 mm thick 1BA according to the standard ISO 527-1993 (E).

2.5. Melt viscosity

The rheological data was recorded using Physica MCR 301 rotational rheometer (Anton Paar GmbH, Austria). The rheometer was equipped with CTD 450 convection heated oven and 25 mm parallel plates geometry, and measurements were conducted at 210 °C under nitrogen atmosphere.

The measurements consisted of frequency sweeps at angular frequencies (ω) from 628 to 0.1 rad/s with a strain of 0.5%, i.e. well within the linear viscoelastic region. The stability of the sample over the course of the measurement was verified by running a short time sweep measurement, $\omega = 1$ rad/s, strain 0.5%, prior and after the frequency sweep.

2.6. Thermal properties

In order to study the effect of NFC on the mobility of the polymer matrix, the glass transition temperatures (T_g) of the composites were determined. The analyses were performed on a Star DSC 821e equipment from Mettler-Toledo, Inc. (Columbus, OH, USA). Samples of the injection molded specimen were heated twice from 25 to 160 °C at a rate of 20 °C/min, and the T_g values were determined during the second heating period. The results were averaged from three samples of each composite to compensate the effect of possible inhomogeneity.

2.7. Optical properties

The appearance and homogeneity of the composite films were evaluated visually and the transparency was measured by spectrophotometry in the wavelength range of 400–700 nm with a Helios β UV/VIS spectrometer from Unicam, Inc. (UK). The results were averaged from three samples of each composite.

Download English Version:

<https://daneshyari.com/en/article/10602735>

Download Persian Version:

<https://daneshyari.com/article/10602735>

[Daneshyari.com](https://daneshyari.com)